APPENDIX D

TECHNICAL BACKGROUND

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D.1   Worst-Case Release Rate for Gases

D.1.1   Unmitigated Release

The assumption that the total quantity of toxic gas is released in 10 minutes is the same assumption used in EPA's *Technical Guidance for Hazards Analysis* (1987).

D.1.2   Gaseous Release Inside Building

The mitigation factor for gaseous release inside a building is based on a document entitled, *Risk Mitigation in Land Use Planning: Indoor Releases of Toxic Gases*, by S.R. Porter. This paper presented three release scenarios and discussed the mitigating effects that would occur in a building with a volume of 1,000 cubic meters at three different building air exchange rates. There is a concern that a building may not be able to withstand the pressures of a very large release. However, this paper indicated that release rates of at least 2,000 pounds per minute could be withstood by a building.

Analyzing the data in this paper several ways, the value of 55 percent emerged as representing the mitigation that could occur for a release scenario into a building. Data are provided on the maximum release rate in a building and the maximum release rate from a building. Making this direct comparison at the lower maximum release rate (3.36 kg/s) gave a release rate from the building of 55 percent of the release rate into the building. Using information provided on another maximum release rate (10.9 kg/min) and accounting for the time for the release to accumulate in the building, approximately 55 percent emerged again.

The choice of building ventilation rates affects the results. The paper presented mitigation for three different ventilation rates, 0.5, 3, and 10 air changes per hour. A ventilation rate of 0.5 changes per hour is representative of specially designed, "gas-tight" buildings, based on the Porter reference. EPA decided that this ventilation rate was appropriate for this analysis. A mitigation factor of 55 percent may be used in the event of a gaseous release which does not destroy the building into which it is released. This factor may overstate the mitigation provided by a building with a higher ventilation rate.

For releases of ammonia, chlorine, and sulfur dioxide, factors specific to the chemicals, the conditions of the release, and building ventilation rates have been developed to estimate mitigation of releases in buildings. For information on these factors and estimation of mitigated release rates, see *Backup Information for the Hazard Assessments in the RMP Offsite Consequence Analysis Guidance, the Guidance for Wastewater Treatment Facilities and the Guidance for Ammonia Refrigeration - Anhydrous Ammonia, Aqueous Ammonia, Chlorine and Sulfur Dioxide*. See also the industry-specific guidance documents for ammonia refrigeration and POTWs.

D.2   Worst-Case Release Rate for Liquids

D.2.1   Evaporation Rate Equation

The equation for estimating the evaporation rate of a liquid from a pool is from the *Technical Guidance for Hazards Analysis*, Appendix G. The same assumptions are made for determination of

maximum pool area (i.e., the pool is assumed to be 1 centimeter (0.033 feet) deep). The evaporation rate equation has been modified to include a different mass transfer coefficient for water, the reference compound. For this document, a value of 0.67 centimeters per second is used as the mass transfer coefficient, instead of the value of 0.24 cited in the *Technical Guidance for Hazards Analysis*. The value of 0.67 is based on Donald MacKay and Ronald S. Matsugu, "Evaporation Rates of Liquid Hydrocarbon Spills on Land and Water," *Canadian Journal of Chemical Engineering*, August 1973, p. 434. The evaporation equation becomes:

$$QR = \frac{0.284 \times U^{0.78} \times MW^{2/3} \times A \times VP}{82.05 \times T} \tag{D-1}$$

where:

	QR	=	Evaporation rate (pounds per minute)
	U	=	Wind speed (meters per second)
	MW	=	Molecular weight (given in Exhibits B-1 and B-2, Appendix B, for toxic substances and Exhibits C-2 and C-3, Appendix C, for flammable substances)
	A	=	Surface area of pool formed by the entire quantity of the mixture (square feet) (determined as described in Section 3.2.2 of the text)
	VP	=	Vapor pressure (mm Hg)
	T	=	Temperature of released substance (Kelvin (K); temperature in ºC plus 273, or 298 for 25 ºC)

D.2.2 Factors for Evaporation Rate Estimates

Liquid Factors. The liquid factors, Liquid Factor Ambient (LFA) and Liquid Factor Boiling (LFB), used to estimate the evaporation rate from a liquid pool (see Section 3.2 of this guidance document), are derived as described in the *Technical Guidance for Hazards Analysis*, Appendix G, with the following differences:

- The mass transfer coefficient of water is assumed to be 0.67, as discussed above; the value of the factor that includes conversion factors, the mass transfer coefficient for water, and the molecular weight of water to the one-third power, given as 0.106 in the *Technical Guidance* is 0.284 in this guidance.

- Density of all substances was assumed to be the density of water in the *Technical Guidance*; the density was included in the liquid factors. For this guidance document, density is not included in the LFA and LFB values presented in the tables; instead, a separate Density Factor (DF) (discussed below) is provided to be used in the evaporation rate estimation.

With these modifications, the LFA is:

$$LFA = \frac{0.284 \times MW^{2/3} \times VP}{82.05 \times 298} \tag{D-2}$$

where: MW =   Molecular weight

	VP	=	Vapor pressure at ambient temperature (mm Hg)
	298 K (25 °C)	=	Ambient temperature and temperature of released substance

LFB is:

$$LFB = \frac{0.284 \times MW^{2/3} \times 760}{82.05 \times BP} \tag{D-3}$$

where:

	MW	=	Molecular weight
	760	=	Vapor pressure at boiling temperature (mm Hg)
	BP	=	Boiling point (K)

LFA and LFB values were developed for all toxic and flammable regulated liquids, and LFB values, to be used for analysis of gases liquefied by refrigeration, were developed for toxic and flammable gases.

Density Factor. Because some of the regulated liquids have densities very different from that of water, the density of each substance was used to develop a Density Factor (DF) for the determination of maximum pool area for the evaporation rate estimation. DF values were developed for toxic and flammable liquids at ambient temperature and for toxic and flammable gases at their boiling points. The density factor is:

$$DF = \frac{1}{d \times 0.033} \tag{D-4}$$

where:

	DF	=	Density factor ($1/(lbs/ft^2)$)
	d	=	Density of the substance in pounds per cubic foot
	0.033	=	Depth of pool for maximum area (feet)

Temperature Correction Factors. Temperature correction factors were developed for toxic liquids released at temperatures above 25 °C, the temperature used for development of the LFAs. The temperature correction factors are based on vapor pressures calculated from the coefficients provided in *Physical and Thermodynamic Properties of Pure Chemicals, Data Compilation*, developed by the Design Institute for Physical Property Data (DIPPR), American Institute of Chemical Engineers. The factors are calculated as follows:

$$TCF_T = \frac{VP_T \times 298}{VP_{298} \times T} \tag{D-5}$$

where:

	TCF_T	=	Temperature Correction Factor at temperature T
	VP_T	=	Vapor pressure at temperature T
	VP_{298}	=	Vapor pressure at 298 K
	T	=	Temperature (K) of released substance

Factors were developed at intervals of 5 °C for temperatures up to 50 °C.

No correction factor was deemed necessary for changes in the density of the regulated toxic liquids with changes in temperature, although the density could affect the pool area and release rate estimates. Analysis of the temperature dependence of the density of these liquids indicated that the changes in density with temperature were very small compared to the changes in vapor pressure with temperature.

D.2.3 Common Water Solutions and Oleum

Water solutions of regulated toxic substances must be analyzed somewhat differently from pure toxic liquids. Except for solutions of relatively low concentration, the evaporation rate varies with the concentration of the solution. At one specific concentration, the composition of the liquid does not change as evaporation occurs. For concentrated solutions of volatile substances, the evaporation rate from a pool may decrease, very rapidly in some cases, as the toxic substance volatilizes and its concentration in the pool decreases. To analyze these changes, EPA used spreadsheets to estimate the vapor pressure, concentration, and release rate at various time intervals for regulated toxic substances in water solution evaporating from pools. In addition to the spreadsheet analysis, EPA used the ALOHA model with an additional step-function feature (not available in the public version). With this step-function feature, changes in the release rate could be incorporated and the effects of these changes on the consequence distance analyzed. The results of the spreadsheet calculations and the model were found to be in good agreement. The distance results obtained from the spreadsheet analysis and the model for various solutions were compared with the results from various time averages to examine the sensitivity of the results. An averaging time of 10 minutes was found to give reasonable agreement with the step-function model for most substances at various concentrations. The spreadsheet analysis also indicated that the first 10 minutes of evaporation was the most important, and the evaporation rate in the first 10 minutes likely could be used to estimate the distance to the endpoint.

Oleum is a solution of sulfur trioxide in sulfuric acid. Sulfur trioxide evaporating from oleum exhibits release characteristics similar to those of toxic substances evaporating from water solutions. Analysis of oleum releases, therefore, was carried out in the same way as for water solutions.

NOAA developed a computerized calculation method to estimate partial vapor pressures and release rates for regulated toxic substance in solution as a function of concentration, based on vapor pressure data from *Perry's Chemical Engineers' Handbook* and other sources. Using this method and spreadsheet calculations, EPA estimated partial vapor pressures and evaporation rates at one-minute intervals over 10 minutes for solutions of various concentrations. The 10-minute time period was chosen based on the ALOHA results and other calculations. For each one-minute interval, EPA estimated the concentration of the solution based on the quantity evaporated in the previous interval and estimated the partial vapor pressure based on the concentration. These estimated vapor pressures were used to calculate an average vapor pressure over the 10-minute period; this average vapor pressure was used to derive Liquid Factor Ambient (LFA) values, as described above for liquids. Use of these factors is intended to give an evaporation rate that accounts for the decrease in evaporation rate expected to take place as the solution evaporates.

Density Factors (DF) were developed for solutions of various concentrations from data in *Perry's Chemical Engineers' Handbook* and other sources, as discussed above for liquids.

Because solutions do not have defined boiling points, EPA did not develop Liquid Factor Boiling (LFB) values for solutions. As a simple and conservative approach, the quantity of a regulated substance in a solution at an elevated temperatures is treated as a pure substance. The LFB for the pure substance, or the

LFA and a temperature correction factor, is used to estimate the initial evaporation rate of the regulated substance from the solution. Only the first 10 minutes of evaporation are considered, as for solutions at ambient temperatures, because the release rate would decrease rapidly as the substance evaporates and the concentration in the solution decreases. This approach will likely give an overestimate of the release rate and of the consequence distance.

D.2.4   Releases Inside Buildings

If a liquid is released inside a building, its release to the outside air will be mitigated in two ways. First, the evaporation rate of the liquid may be much lower inside a building than outside. This is due to wind speed, which directly affects the evaporation rate. The second mitigating factor is that the building provides resistance to discharge of contaminated air to the outdoors.

In this method, a conservative wind speed, U, of 0.1 meter per second (m/s) was assumed in the building. (See end of text for a justification of this wind speed.) For a release outdoors in a worst-case scenario, U is set to 1.5 m/s, and for an alternative scenario, U is set to 3 m/s. The evaporation rate equation is:

$$QR = U^{0.78} \times (LFA, \ LFB) \times A \tag{D-6}$$

where: QR =   Release rate (pounds per minute (lbs/min))
             U =   Wind speed (meters per second (m/s))
             LFA =   Liquid Factor Ambient
             LFB =   Liquid Factor Boiling
             A =   Area of pool (square feet (ft^2))

As can be seen, if U inside a building is only 0.1, then the evaporation rate inside a building will be much lower than a corresponding evaporation rate outside (assuming the temperature is the same). The rate will only be $(0.1/1.5)^{0.78}$, about 12 percent of the rate for a worst case, and $(0.1/3)^{0.78}$, about seven percent of the rate for an alternative case.

The evaporated liquid mixes with and contaminates the air in the building. What EPA is ultimately interested in is the rate at which this contaminated air exits the building. In order to calculate the release of contaminated air outside the building, EPA adapted a method from an UK Health and Safety Executive paper entitled, *Risk Mitigation in Land Use Planning: Indoor Releases of Toxic Gases*, by S.R. Porter. EPA assumed that the time for complete evaporation of the liquid pool was one hour. The rate at which contaminated air was released from the building during liquid evaporation (based on the paper) was assumed to be equal to the evaporation rate plus the building ventilation rate (no pressure buildup in building). The building ventilation rate was set equal to 0.5 air changes per hour. This ventilation rate is representative of a specially designed, "gas-tight" building. (The mitigation factor developed based on this type of building would overstate the mitigation provided by a building with higher ventilation rates.) EPA used a building with a volume of 1,000 cubic meters (m^3) and a floor area of 200 m^2 (2,152 ft^2) as an example for this analysis. EPA assumed that the liquid pool would cover the entire building floor, representing a conservative scenario.

To provide a conservative estimate, EPA calculated the evaporation rate for a spill of a volatile liquid, carbon disulfide (CS_2), under ambient conditions inside the building:

$$QR = 0.1^{0.78} \times 0.075 \times 2,152 = 26.8 \text{ pounds per minute (lbs/min)}$$

Next, this evaporation rate was converted to cubic meters per minute (m^3/min) using the ideal gas law (the molecular weight of CS_2 is 76.1):

26.8 lbs/min $\times$ 454 grams per pound (g/lb) $\times$ 1 mole CS_2/76.1 g $\times$ 0.0224 m^3/mole = 3.58 m^3/min.

The ventilation rate of the building is 0.5 changes per hour, which equals 500 m^3 per hour, or 8.33 m^3/min. Therefore, during evaporation, contaminated air is leaving the building at a rate of 8.33 + 3.58, or 11.9 m^3/min.

EPA used an iterative calculation for carbon disulfide leaving a building using the above calculated parameters. During the first minute of evaporation, 26.8 lbs of pure carbon disulfide evaporates, and EPA assumed this evenly disperses through the building so that the concentration of CS_2 in the building air is 0.0268 lbs/m^3 (assuming 1000 m^3 volume in the building). Contaminated air is exiting the building at a rate of 11.9 m^3/min, so EPA deduced that 11.9 $\times$ 0.0268 = 0.319 lbs of carbon disulfide exit the building in the first minute, leaving 26.5 lbs still evenly dispersed inside. Since this release occurs over one minute, the release rate of the carbon disulfide to the outside is 0.319 lbs/min. During the second minute, another 26.8 lbs of pure carbon disulfide evaporates and disperses, so that the building now contains 26.8 + 26.5 = 53.3 lbs of carbon disulfide, or 0.0533 lbs/m^3. Contaminated air is still exiting the building at a rate of 11.9 m^3/min, so 11.9 $\times$ 0.05328 = 0.634 lbs of carbon disulfide are released, leaving 52.6 lbs inside. Again, this release occurs over one minute so that the rate of carbon disulfide exiting the building in terms of contaminated air is 0.634 lbs/min. EPA continued to perform this estimation over a period of one hour. The rate of release of carbon disulfide exiting the building in the contaminated air at the sixty minute mark is 13.7 lbs/min. This represents the maximum rate of carbon disulfide leaving the building. After all of the carbon disulfide is evaporated, there is a drop in the concentration of carbon disulfide in the contaminated air leaving the building because the evaporation of carbon disulfide no longer contributes to the overall contamination of the air.

Note that if the same size pool of carbon disulfide formed outside, the release rate for a worst-case scenario would be:

$$QR = 1.5^{0.78} \times 0.075 \times 2,152 = 221 \text{ lbs/min.}$$

and for an alternative case:

$$QR = 3^{0.78} \times 0.075 \times 2,152 = 380 \text{ lbs/min.}$$

The maximum release rate of carbon disulfide in the contaminated building air, assuming a 1,000 m^3 building with a building exchange rate of 0.5 air changes per hour, was only about 6 percent (13.7 ÷ 221 lbs/min x 100) of the worst-case scenario rate, and only about 3.6 percent (13.7 ÷ 380 lbs/min x 100) of the alternative scenario rate. EPA set an overall building mitigation factor equal to 10 percent and five percent, respectively, in order to be conservative. Please note that (at a constant ventilation rate of 0.5 changes per

hour) as the size of the building increases, the maximum rate of contaminated air leaving the building will decrease, although only slightly, because of the balancing effect of building volume and ventilation rate. Obviously, a higher ventilation rate will yield a higher maximum release rate of contaminated air from the building.

For a release inside a building, EPA assumed a building air velocity of 0.1 m/s. This conservative value was derived by setting the size of the ventilation fan equal to 1.0 m^2. This fan is exchanging air from the building with the outside at a rate of 0.5 changes per hour. For a 1,000 m^3 building, this value becomes 500 m^3/hour, or 0.14 m^3/s. Dividing 0.14 m^3/s by the area of the fan yields a velocity of 0.14 m/s, which was rounded down to 0.1 m/s.

D.3   Toxic Endpoints

The toxic endpoints for regulated toxic substances, which are specified in the RMP Rule, are presented in Appendix B, Exhibits B-1, B-2, and B-3. The endpoints were chosen as follows, in order of preference:

(1)   Emergency Response Planning Guideline 2 (ERPG-2), developed by the American Industrial Hygiene Association, if available;

(2)   Level of Concern (LOC) derived for extremely hazardous substances (EHSs) regulated under section 302 of the Emergency Planning and Community Right-to-Know Act (EPCRA) (see the *Technical Guidance for Hazards Analysis* for more information on LOCs); the LOC for EHSs is based on:

--   One-tenth of the Immediately Dangerous to Life and Health (IDLH) level, developed by the National Institute of Occupational Safety and Health (NIOSH), using IDLH values developed before 1994,

or, if no IDLH value is available,

--   One-tenth of an estimated IDLH derived from toxicity data; the IDLH is estimated as described in Appendix D of the *Technical Guidance for Hazards Analysis*.

Note that the LOCs were not updated using IDLHs published in 1994 and later, because NIOSH revised its methodology for the IDLHs. The EHS LOCs based on earlier IDLHs were reviewed by EPA's Science Advisory Board, and EPA decided to retain the methodology that was reviewed.

ERPG-2 is defined as the maximum airborne concentration below which it is believed nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms that could impair an individual's ability to take protective action.

IDLH (pre-1994) concentrations were defined in the NIOSH *Pocket Guide to Chemical Hazards* as representing the maximum concentration from which, in the event of respirator failure, one could escape within 30 minutes without a respirator and without experiencing any escape-impairing (e.g., severe eye

irritation) or irreversible health effects. (As noted above, LOCs for EHSs were not updated to reflect 1994 and later IDLHs.)

The estimated IDLH is derived from animal toxicity data, in order of preferred data, as follows:

- From median lethal concentration (LC_{50}) (inhalation): 0.1 x LC_{50}

- From lowest lethal concentration (LC_{LO}) (inhalation): 1 x LC_{LO}

- From median lethal dose (LD_{50}) (oral): 0.01 x LD_{50}

- From lowest lethal dose (LD_{LO}) (oral): 0.1 x LD_{LO}

The toxic endpoints based on LOCs for EHSs presented in the tables in Appendix B are, in some cases, different from the LOCs listed in the *Technical Guidance for Hazards Analysis*, because some of the LOCs were updated based on IDLHs that were published after the development of the LOCs (and before 1994) or on new or revised toxicity data.

D.4 Reference Tables for Distances to Toxic and Flammable Endpoints

D.4.1 Neutrally Buoyant Gases

Toxic Substances. Reference tables for distances to toxic endpoints for neutrally buoyant gases and vapors were derived from the Gaussian model using the longitudinal dispersion coefficients based on work by Beals (*Guide to Local Diffusion of Air Pollutants*, Technical Report 214. Scott Air Force Base, Illinois: U.S. Air Force, Air Weather Service, 1971). The reasons for using the Beals dispersion coefficients are discussed below.

Longitudinal dispersion (dispersion in the along-wind direction) is generated mostly by vertical wind shear. Wind shear results from the tendency of the wind speed to assume a wind profile—the speed is lowest next to the ground and increases with height until it reaches an asymptotic value at approximately a few hundred feet above the surface. To account for shear-driven dispersion, any air dispersion model intended for modeling short-duration releases must include either (a) a formulation that accounts, either implicitly or explicitly, for the height-dependence of wind speed or (b) some type of parameterization that converts shear effect into σ_x, the standard deviation function in the along-wind direction.

Because the standard Gaussian formula does not incorporate σ_x (it includes only σ_y and σ_z, the crosswind and horizontal functions), very few alternate ways to formulate σ_x have been proposed. The simplest method was proposed by Turner (*Workbook of Atmospheric Dispersion Estimates*, Report PB-191 482. Research Triangle Park, North Carolina: Office of Air Programs, U.S. Environmental Protection Agency, 1970), who suggested simply setting σ_x equal to σ_y. Textbooks such as that by Pasquill and Smith (*Atmospheric Diffusion*, 3rd ed. New York: Halstead Press, 1983) describe a well-known analytic model. However, this model is more complex than a Gaussian model because according to it, dispersion depends on wind shear and the vertical variation of the vertical diffusion coefficient. Wilson (Along-wind Diffusion of Source Transients, *Atmospheric Environment* 15:489-495, 1981) proposed another method in which σ_x is

determined as a function of wind shear, but in a form that can then be used in a Gaussian model. However, it is now believed that Wilson's formulation gives σ_x values that are too large.

To avoid the problems of the analytic method and Wilson's formulation, we chose to include a formulation for σ_x derived from work by Beals (1971). We had three reasons for doing so. First, in terms of magnitude, Beals' σ_x fell in the midrange of the alternative formulations that we reviewed. Second, Beals' σ_x indirectly accounts for wind shear by using (unpublished) experimental data. Third, both the ALOHA and DEGADIS models incorporate the Beals methodology.

When a substance is dispersed downwind, the concentration in the air changes over time. To assess the health effects of potential exposure to the substance, the average concentration of the substance over some time period is determined. Averaging time is the time interval over which the instantaneous concentration of the hazardous material in the vapor cloud is averaged. Averaging time should generally be equal to or shorter than either the release duration or cloud duration and, if possible, should reflect the exposure time associated with the toxic exposure guideline of interest. The exposure time associated with the toxic endpoints specified under the RMP Rule include 30 minutes for the Immediately Dangerous to Life and Health (IDLH) level and 60 minutes for the Emergency Response Planning Guideline (ERPG). For the neutrally buoyant tables, the 10-minute release scenario was modeled using a 10-minute averaging time. The 60-minute release scenario was modeled using a 30-minute averaging time to be consistent with the 30-minute exposure time associated with the IDLH. A 60-minute averaging time may have underpredicted consequence distances and, therefore, was not used for development of the distance tables for this guidance.

Cloud dispersion from a release of finite duration (10 and 60-minute releases) is calculated using an equation specified in the NOAA publication *ALOHA^{TM} 5.0 Theoretical Description*, Technical Memorandum NOS ORCA 65, August 1992.

Flammable Substances. The reference tables of distances for vapor cloud fires of neutrally buoyant flammable substances were derived using the same model as for toxic substances, as described above. The endpoint for modeling was the lower flammability limit (LFL). For flammable substances, an averaging time of 0.1 minute (six seconds) was used, because fires are considered to be nearly instantaneous events.

Distances of interest for flammable substances are generally much shorter than for toxic substance, because the LFL concentrations are much larger than the toxic endpoints. For the short distances found in modeling the flammable substances, modeling results were found to be the same for 10-minute and longer releases; therefore, one table of distances for rural conditions and one table for urban conditions, applicable for both 10-minute and longer releases, were developed for flammable substances.

D.4.2 Dense Gases

Toxic Substances. The reference tables for dense gases were developed using the widely accepted SLAB model, developed by Lawrence Livermore National Laboratory. SLAB solves conservation equations of mass, momentum, energy, and species for continuous, finite duration, and instantaneous releases. The reference tables were based on the evaporating pool algorithm.

For the reference tables were developed based on modeling releases of hydrogen chloride (HCl). HCl was chosen based on a SLAB modeling analysis of a range of dispersion behavior for releases of regulated

dense gases or vapors with different molecular weights. This analysis showed that releases of HCl generally provided conservative results under a variety of stability/wind speed combinations, release rates, and toxic endpoints.

Similar to the modeling of neutrally buoyant plumes, the 10-minute release scenario of toxic chemicals was modeled using a 10-minute averaging time. The 60-minute release scenario was modeled using a 30-minute averaging time to be consistent with the 30-minute exposure time associated with the IDLH.

For all dense gas tables, the reference height for the wind speed was 10 meters. Relative humidity was assumed to be 50 percent, and the ambient temperature was 25 ºC. The source area was the smallest value that still enabled the model to run for all release rates. The surface roughness factor was one meter for urban scenarios and three centimeters for rural scenarios.

Flammable Substances. For the reference tables for dispersion of dense flammable gases and vapors, for analysis of vapor cloud fires, the same model was used as for toxic substances, as described above, and the same assumptions were made. For the dispersion of flammable chemicals, averaging time should be very small (i.e., no more than a few seconds), because flammable vapors need only be exposed to an ignition source for a short period of time to initiate the combustion process. Thus, both the 10-minute and 60-minute reference tables for flammable substances use an averaging time of 10 seconds. The 10-minute and 60-minute tables were combined for flammable substances because the modeling results were found to be the same.

D.4.3 Chemical-Specific Reference Tables

The chemical-specific reference tables of distances for ammonia, chlorine, and sulfur dioxide were developed for EPA's risk management program guidance for ammonia refrigeration and for POTWs. For information on the chemical-specific modeling and development of the chemical-specific reference tables, see *Backup Information for the Hazard Assessments in the RMP Offsite Consequence Analysis Guidance, the Guidance for Wastewater Treatment Facilities and the Guidance for Ammonia Refrigeration - Anhydrous Ammonia, Aqueous Ammonia, Chlorine and Sulfur Dioxide*. See also the industry-specific guidance documents for ammonia refrigeration and POTWs.

The modeling carried out for aqueous ammonia also is applied in this guidance to ammonia released as a neutrally buoyant plume in other situations. The tables of distances derived from this modeling would apply to evaporation of ammonia from a water solution, evaporation of ammonia liquefied by refrigeration, or ammonia releases from the vapor space of a vessel, because the ammonia would behave as a neutrally buoyant plume (or possibly buoyant in some cases).

D.4.4 Choice of Reference Table for Dispersion Distances

Gases. Exhibit B-1 of Appendix B indicates whether the reference tables for neutrally buoyant or dense gases should be used for each of the regulated toxic gases. Exhibit C-2, Appendix C, provides this information for flammable gases. The choice of reference table presented in these exhibits is based on the molecular weight of the regulated substance compared to air; however, a number of factors that may cause a substance with a molecular weight similar to or smaller than the molecular weight of air to behave as a dense

gas should be considered in selecting the appropriate table. For example, a cold gas may behave as a dense gas, even if it is lighter than air at ambient temperature. Gases liquefied under pressure may be released as a mixture of vapor and liquid droplets; because of presence of liquid mixed with the vapor, a gas that is lighter than air may behave as a dense gas in such a release. A gas that polymerizes or forms hydrogen bonds (e.g., hydrogen fluoride) also may behave as a dense gas.

Liquids and Solutions. Exhibits B-2 and B-3, Appendix B, and Exhibit C-3, Appendix C, indicate the reference table of distances to be used for each regulated liquid. The methodology presented in this guidance for consequence analysis for liquids and solutions assumes evaporation from a pool. All of the liquids regulated under CAA section 112(r) have molecular weights greater than the molecular weight of air; therefore, their vapor would be heavier than air. However, because the vapor from a pool will mix with air as it evaporates, the initial density of the vapor with respect to air may not in all cases indicate whether the vapor released from a pool should be modeled as a dense gas or a neutrally buoyant gas. If the rate of release from the pool is relatively low, the vapor-air mixture that is generated may be neutrally buoyant even if the vapor is denser than air, because the mixture may contain a relatively small fraction of the denser-than-air vapor; i.e., it may be mostly air. This may be the case particularly for some of the regulated toxic liquids with relatively low volatility. All of the regulated flammable substances have relatively high volatility; the reference tables for dense gases are assumed to be appropriate for analyzing dispersion of these flammable liquids.

To identify toxic liquids with molecular weight greater than air that might behave as neutrally buoyant gases when evaporating from a pool, EPA used the ALOHA model for pool evaporation of a number of substances with a range of molecular weights and vapor pressures. Modeling was carried out for F stability and wind speed 1.5 meters per second (worst-case conditions) and for D stability and wind speed 3.0 meters per second (alternative-case conditions). Pool spread to a depth of one centimeter was assumed. Additional modeling was carried out for comparison assuming different pool areas and depths. The molecular weight-vapor pressure combinations at which ALOHA used the neutrally buoyant gas model were used to develop the reference table choices given in Exhibit B-2 (for liquids) and B-3 (for solutions) in Appendix B. The neutrally buoyant tables should generally give reasonable results for pool evaporation under ambient conditions when indicated for liquids. At elevated temperatures, however, evaporation rates will be greater, and the dense gas tables should be used.

The liquids for which the neutrally buoyant table is identified for the worst case probably can be expected to behave as neutrally buoyant vapors when evaporating from pools under ambient conditions in most situations, but there may be cases when they exhibit dense gas behavior. Other liquids, for which the neutrally buoyant tables are not indicated for the worst case, might release neutrally buoyant vapors under some conditions (e.g., relatively small pools, temperature not much above 25 °C). Similarly, the liquids for which the neutrally buoyant tables are indicated as appropriate for alternative scenario analysis probably can be considered to behave as neutrally buoyant vapors under the alternative scenario conditions in most cases; however, there may be cases where they will behave as dense gases, and there may be other liquids that in some cases would exhibit neutrally buoyant behavior when evaporating. The reference table choices shown in Exhibit B-2 are intended to reflect the most likely behavior of the substances; they will not predict behavior of the listed substances evaporating under all conditions.

D.4.5   Additional Modeling for Comparison

Modeling was carried out for two worst-case examples and two alternative-case examples, using two different models, for comparison with the results obtained from the methods and distance tables in this guidance. This modeling is discussed below.

ALOHA Model. The Areal Locations of Hazardous Atmospheres (ALOHA) system was developed jointly by NOAA and EPA. ALOHA Version 5.2.1 was used for the comparison modeling. The parameters for ALOHA modeling were the same as specified in this guidance document for worst-case and alternative scenarios. The substances modeled are included in ALOHA's chemical database, so no chemical data were entered for modeling. For consistency with the methodology used to develop the reference tables of distances, a wind speed height of 10 meters was selected for ALOHA modeling.

For all of the substances modeled, the direct source model was chosen for ALOHA modeling, and the release rate estimated using the guidance methodology was entered as the release rate for ALOHA. ALOHA selected the dense gas model to estimate the distances to the endpoints in all cases.

WHAZAN Model. The World Bank Hazard Analysis (WHAZAN) system was developed by Technica International in collaboration with the World Bank. The 1988 version of WHAZAN was used for the comparison modeling. The parameters for atmospheric stability, wind speed, and ambient temperature and humidity were the same as specified in this guidance document. For surface roughness, WHAZAN requires entry of a "roughness parameter," rather than a height. Based on the discussion of this parameter in the WHAZAN Theory Manual, a roughness parameter of 0.07 (corresponding to flat land, few trees) was chosen as equivalent to the surface roughness of 3 centimeters used to represent rural topography in modeling to develop the distance tables for this guidance. A roughness parameter of 0.17 (for woods or rural area or industrial site) was chosen as equivalent to 1 meter, which was used to develop the urban distance tables. Data were added to the WHAZAN chemical database for acrylonitrile and allyl alcohol; ethylene oxide and chlorine were already included in the database.

For WHAZAN modeling of the gases ethylene oxide and chlorine and the liquid acrylonitrile, the WHAZAN dense cloud dispersion model was used. For the alternative-case release of allyl alcohol, the buoyant plume dispersion model was used for consistency with the guidance methodology. The release rates estimated using the guidance methodology were entered as the release rates for all of the WHAZAN modeling.

The WHAZAN dense cloud dispersion requires a "volume dilution factor" as one of its inputs. This factor was not explained; it was presumed to account for dilution of pressurized gases with air upon release. For the gases modeled, the default dilution factor of 60 was used; for acrylonitrile, a dilution factor of 0 was entered. This factor appears to have little effect on the distance results.

D.5   Worst-Case Consequence Analysis for Flammable Substances

The equation used for the vapor cloud explosion analysis for the worst case involving flammable substances is given in Appendix C. This equation is based on the TNT-equivalency method of the UK Health and Safety Executive, as presented in the publication of the Center for Chemical Process Safety of the American Institute of Chemical Engineers (AIChE), *Guidelines for Evaluating the Characteristics of Vapor*

Cloud Explosions, Flash Fires, and BLEVEs (1994). The assumption was made for the worst case that the total quantity of the released substance is in the flammable part of the cloud. The AIChE document lists this assumption as one of a number that have been used for vapor cloud explosion blast prediction; it was chosen as a conservative assumption for the worst-case analysis. The yield factor of 10 percent was a conservative worst-case assumption, based on information presented in the AIChE document. According to the AIChE document, reported values for TNT equivalency for vapor cloud explosions range from a fraction of one percent to tens of percent; for most major vapor cloud explosions, the range is one to ten percent.

The endpoint for the vapor cloud explosion analysis, 1 psi, is reported to cause damage such as shattering of glass windows and partial demolition of houses. Skin laceration from flying glass also is reported. This endpoint was chosen for the consequence analysis because of the potential for serious injuries to people from the property damage that might result from an explosion.

The TNT equivalent model was chosen as the basis for the consequence analysis because of its simplicity and wide use. This model does not take into account site-specific factors and many chemical-specific factors that may affect the results of a vapor cloud explosion. Other methods are available for vapor cloud explosion modeling; see the list of references in Appendix A for some publications that include information on other vapor cloud explosion modeling methods.

D.6   Alternative Scenario Analysis for Gases

The equation for estimating release rate of a gas from a hole in a tank is based on the equations for gas discharge rate presented in the *Handbook of Chemical Hazard Analysis Procedures* by the Federal Emergency Management Agency (FEMA), DOT, and EPA, and equations in EPA's *Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants*. The equation for an instantaneous discharge under non-choked flow conditions is:

$$m = C_d\, A_h\, \sqrt{2 p_0 \rho_0 \left(\frac{\gamma}{\gamma-1} \right) \left[\left(\frac{p_1}{p_0} \right)^{\frac{2}{\gamma}} - \left(\frac{p_1}{p_0} \right)^{\frac{\gamma+1}{\gamma}} \right]} \qquad \textbf{(D-7)}$$

where:

m	=	Discharge rate (kg/s)
C_d	=	Discharge coefficient
A_h	=	Opening area (m^2)
γ	=	Ratio of specific heats
p_0	=	Tank pressure (Pascals)
p_1	=	Ambient pressure (Pascals)
ρ_0	=	Density (kg/m^3)

Under choked flow conditions (maximum flow rate), the equation becomes:

$$m = C_d\, A_h\, \sqrt{\gamma p_0 \rho_0 \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \qquad \textbf{(D-8)}$$

For development of the equation and gas factors presented in this guidance, density (ρ) was rewritten as a function of pressure and molecular weight, based on the ideal gas law:

$$\rho = \frac{p_0\, MW}{R\, T_t} \qquad \textbf{(D-9)}$$

where:

MW	=	Molecular weight (kilograms per kilomole)
R	=	Gas constant (8,314 Joules per degree-kilomole)
T_t	=	Tank temperature (K)

The choked flow equation can be rewritten:

$$m = C_d\, A_h\, p_0\, \frac{1}{\sqrt{T_t}} \sqrt{\gamma \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \sqrt{\frac{MW}{8314}} \qquad \textbf{(D-10)}$$

To derive the equation presented in the guidance, all the chemical-specific properties, constants, and appropriate conversion factors were combined into the "Gas Factor" (GF). The discharge coefficient was assumed to have a value of 0.8, based on the screening value recommended in EPA's *Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants*. The GF was derived as follows:

$$GF = 132.2 \times 6{,}895 \times 6.4516 \times 10^{-4} \times 0.8 \sqrt{\gamma \left(\frac{2}{\gamma+1}\right)^{\frac{\gamma+1}{\gamma-1}}} \sqrt{\frac{MW}{8314}} \qquad \textbf{(D-11)}$$

where:

132.2	=	Conversion factor for lbs/min to kg/s
6,895	=	Conversion factor for psi to Pascals (p_0)
6.4516×10^{-4}	=	Conversion factor for square inches to square meters (A_h)

GF values were calculated for all gases regulated under CAA section 112(r) and are listed in Appendix B, Exhibit B-1, for toxic gases and Appendix C, Exhibit C-2, for flammable gases.

From the equation for choked flow above and the equation for the GF above, the initial release rate for a gas from a hole in a tank can be written as:

$$QR = HA \times P_t \times \frac{1}{\sqrt{T_t}} \times GF \qquad \textbf{(D-12)}$$

where:
QR	=	Release rate (pounds per minute)
HA	=	Hole area (square inches)
P_t	=	Tank pressure (psia)
T_t	=	Tank temperature (K)

D.7 Alternative Scenario Analysis for Liquids

D.7.1 Releases from Holes in Tanks

The equation for estimating release rate of a liquid from a hole in a tank is based on the equations for liquid release rate presented in the *Handbook of Chemical Hazard Analysis Procedures* by FEMA, DOT, and EPA and EPA's *Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants*. The equation for the instantaneous release rate is:

$$m = A_h C_d \sqrt{\rho_l \left[2g\rho_l \left(H_L - H_h \right) + 2 \left(P_0 - P_a \right) \right]} \qquad \textbf{(D-13)}$$

where:
m	=	Discharge rate (kilograms per second)
A_h	=	Opening area (square meters)
C_d	=	Discharge coefficient (unitless)
g	=	Gravitational constant (9.8 meters per second squared)
ρ_l	=	Liquid density (kilograms per cubic meter)
P_0	=	Storage pressure (Pascals)
P_a	=	Ambient pressure (Pascals)
H_L	=	Liquid height above bottom of container (meters)
H_h	=	Height of opening (meters)

A version of this equation is presented in the guidance for use with data found in Appendix B, for gases liquefied under pressure. The equation in the text was derived using the conversion factors listed below and density factors and equilibrium vapor pressure or tank pressure values listed in Appendix B, Exhibit B-1. Equation D-13 becomes:

$$QR = 132.2 \times 6.4516 \times 10^{-4} \times 0.8 \times HA \sqrt{16.018 \times d \times [2 \times 9.8 \times 16.018 \times d \times LH \times 0.0254 + 2P_g \times 6895]} \qquad \textbf{(D-14)}$$

where:

QR	=	Release rate (pounds per minute)	
HA	=	Hole area (square inches)	
132.2	=	Conversion factor for kilograms per second to pounds per minute	
6.4516×10^{-4}	=	Conversion factor for square inches to square meters (HA)	
0.8	=	Discharge coefficient (0.8)	
d	=	Liquid density (pounds per cubic foot); can derived by using the density factor: 1/(DFx0.033)	
16.018	=	Conversion factor for pounds per cubic feet to kilograms per cubic meters (D)	
9.8	=	Gravitational constant (meters per second squared)	
LH	=	Height of liquid above hole (inches)	
2.54×10^{-2}	=	Conversion factor for inches to meters (LH)	
P_g	=	Gauge pressure in tank (psi)	
6,895	=	Conversion factor for psi to Pascals (P_g)	

After combining the conversion factors and incorporating the density factor (DF), this equation becomes:

$$QR = HA \times 6.82 \sqrt{\frac{0.7}{DF^2} \times LH + \frac{669}{DF} \times P_g} \qquad \textbf{(D-15)}$$

For liquids stored at ambient pressure, Equation D-13 becomes:

$$m = A_h C_d \rho_l \sqrt{2g \left(H_L - H_h\right)} \qquad \textbf{(D-16)}$$

To derive the equation presented in the guidance for liquids under ambient pressure, all the chemical-specific properties, constants, and conversion factors were combined into the "Liquid Leak Factor" (LLF). The discharge coefficient was assumed to have a value of 0.8, based on the screening value recommended in EPA's *Workbook of Screening Techniques for Assessing Impacts of Toxic Air Pollutants*. The LLF was derived as follows:

$$LLF = 132.2 \times 6.4516 \times 10^{-4} \times 0.1594 \times 0.8 \times \sqrt{2 \times 9.8} \times \rho_l \qquad \textbf{(D-17)}$$

where:

LLF	=	Liquid Leak Factor (pounds per minute-inches$^{2.5}$)
132.2	=	Conversion factor for kilograms per second to pounds per minute (m)
6.4516×10^{-4}	=	Conversion factor for square inches to square meters (A_h)
0.1594	=	Conversion factor for square root of inches to square root of meters (H_L - H_h)
0.8	=	Discharge coefficient (0.8)
9.8	=	Gravitational constant (meters per second squared)
ρ_l	=	Liquid density (kilograms per cubic meter)

LLF values were calculated for all liquids regulated under CAA section 112(r) and are listed in Appendix B, Exhibit B-2, for toxic liquids and Appendix C, Exhibit C-3, for flammable liquids.

From the equation for liquid release rate from a hole in a tank at ambient pressure and the equation for the LLF, the initial release rate for a liquid from a tank under atmospheric pressure can be written as:

$$QR_L = HA \times \sqrt{LH} \times LLF \tag{D-18}$$

where:

QR_L	=	Liquid release rate (pounds per minute)
HA	=	Hole area (square inches)
LH	=	Height of liquid above hole (inches)

D.7.2 Releases from Pipes

The equation used to estimate releases of liquids from pipes is the Bernoulli equation. It assumes that the density of the liquid is constant and does not account for losses in velocity due to wall friction. The equation follows:

$$\frac{(P_a - P_b)}{D} + \frac{g\,(Z_a - Z_b)}{g_c} = \frac{(V_b^2 - V_a^2)}{2g_c} \tag{D-19}$$

where:

P_a	=	Pressure at pipe inlet (Pascals)
P_b	=	Pressure at pipe outlet (Pascals)
Z_a	=	Height above datum plane at pipe inlet (meters)
Z_b	=	Height above datum plane at pipe release (meters)
g	=	Gravitational acceleration (9.8 meters per second squared)
g_c	=	Newton's law proportionality factor (1.0)
V_a	=	Operational velocity (meters per second)
V_b	=	Release velocity (meters per second)
D	=	Density of liquid (kilograms per cubic meter)

Isolating V_b yields:

$$V_b = \sqrt{\frac{2\,g_c\,(P_a - P_b)}{D} + 2\,g\,(Z_a - Z_b) + V_a^2} \tag{D-20}$$

To develop the equation presented in the text, conversion factors for English units and constants were incorporated as follows:

$$V_b = 197 \sqrt{\frac{2 \times 6895 \times (P_T - 14.7) \times DF \times 0.033}{16.08} + (2 \times 9.8 \times 0.3048 \times (Z_a - Z_b) + 0.00508^2 \times V_a^2}$$ **(D-21)**

where: V_b = Release velocity (feet per minute)
    197 = Conversion factor for meters per second to feet per minute
    6895 = Conversion factor for psi to Pascals
    P_T = Total pipe pressure (psi)
    14.7 = Atmospheric pressure (psi)
    16.08 = Conversion factor for pounds per cubic foot to kilograms per cubic meter
    DF = Density factor (1/(0.033 DF)= density in pounds per cubic foot)
    9.8 = Gravitational acceleration (meters per second^2)
    0.3048 = Conversion factor for feet to meters
    Z_a-Z_b = Change in pipe elevation, inlet to outlet (feet)
    0.00508= Conversion factor for feet per minute to meters per second
    V_a = Operational velocity (feet per minute)

D.8   Vapor Cloud Fires

Factors for leaks from tanks for flammable substances (GF and LLF) were derived as described for toxic substances (see above).

The endpoint for estimating impact distances for vapor cloud fires of flammable substances is the lower flammability limit (LFL). The LFL is one of the endpoints for releases of flammable substances specified in the RMP Rule. It was chosen to provide a reasonable, but not overly conservative, estimation of the possible extent of a vapor cloud fire.

D.9   Pool Fires

A factor used for estimating the distance to a heat radiation level from a pool fire that could cause second degree burns from a 40-second exposure was developed based on equations presented in the AIChE document, *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs* and in the Netherlands TNO document, *Methods for the Determination of Possible Damage to People and Objects Resulting from Releases of Hazardous Materials* (1992). The AIChE and TNO documents present a point-source model that assumes that a selected fraction of the heat of combustion is emitted as radiation in all directions. The radiation per unit area received by a target at some distance from the point source is given by:

$$q = \frac{f \, m \, H_c \, \tau_a}{4 \pi x^2}$$ **(D-22)**

where:

q	=	Radiation per unit area received by the receptor (Watts per square meter)
m	=	Rate of combustion (kilograms per second)
τ_a	=	Atmospheric transmissivity
H_c	=	Heat of combustion (Joules per kilogram)
f	=	Fraction of heat of combustion radiated
x	=	Distance from point source to receptor (meters)

The fraction of combustion energy dissipated as thermal radiation (f in the equation above) is reported to range from 0.1 to 0.4. To develop factors for estimating distances for pool fires, this fraction was assumed to be 0.4 for all the regulated flammable substances. The heat radiation level (q) was assumed to be 5 kilowatts (5,000 Watts) per square meter. This level is reported to cause second degree burns from a 40-second exposure. One of the endpoints for releases of flammable substances specified in the RMP Rule is 5 kilowatts per square meter for 40 seconds. It was assumed that people would be able to escape from the heat in 40 seconds. The atmospheric transmissivity (τ_a) was assumed equal to one.

For a pool fire of a flammable substance with a boiling point above the ambient temperature, the combustion rate can be estimated by the following empirical equation:

$$m = \frac{0.0010 \, H_c \, A}{H_v + C_p \, (T_b - T_a)} \tag{D-23}$$

where:

m	=	Rate of combustion (kilograms per second)
H_c	=	Heat of combustion (Joules per kilogram)
H_v	=	Heat of vaporization (Joules per kilogram)
C_p	=	Liquid heat capacity (Joules per kilogram-degree K)
A	=	Pool area (square meters)
T_b	=	Boiling temperature (K)
T_a	=	Ambient temperature (K)
0.0010	=	Constant

Combining Equations D-22 and D-23 (above), and assuming a heat radiation level of 5,000 Watts per square meter, gives the following equation for liquid pools of substances with boiling points above ambient temperature:

$$x = H_c \sqrt{0.4 \, \frac{\left(\dfrac{0.0010 \, A}{H_v + C_p(T_b - T_a)} \right)}{4\pi q}} \tag{D-24}$$

or

$$x = H_c \sqrt{\frac{0.0001\ A}{5{,}000\pi\ (H_v + C_p(T_b - T_a))}} \qquad \textbf{(D-25)}$$

where:

x	=	Distance from point source to receptor (meters)	
q	=	Radiation per unit area received by the receptor = 5,000 Watts per square meter	
H_c	=	Heat of combustion (Joules per kilogram)	
f	=	Fraction of heat of combustion radiated = 0.4	
H_v	=	Heat of vaporization (Joules per kilogram)	
C_p	=	Liquid heat capacity (Joules per kilogram-degree Kelvin)	
A	=	Pool area (square meters)	
T_b	=	Boiling temperature (K)	
T_a	=	Ambient temperature (K)	
0.0010	=	Constant	

For a pool fire of a flammable substance with a boiling point below the ambient temperature (i.e., liquefied gases) the combustion rate can be estimated by the following equation, based on the TNO document:

$$m = \frac{0.0010\ H_c\ A}{H_v} \qquad \textbf{(D-26)}$$

where:

m	=	Rate of combustion (kilograms per second)
H_v	=	Heat of vaporization (Joules per kilogram)
H_c	=	Heat of combustion (Joules per kilogram)
A	=	Pool area (square meters)
0.0010	=	Constant

Then the equation for distance at which the radiation received equals 5,000 Watts per square meter becomes:

$$x = H_c \sqrt{\frac{0.0001\ A}{5{,}000\pi\ H_v}} \qquad \textbf{(D-27)}$$

where:

x	=	Distance from point source to receptor (meters)
5,000	=	Radiation per unit area received by the receptor (Watts per square meter)
H_c	=	Heat of combustion (Joules per kilogram)
H_v	=	Heat of vaporization (Joules per kilogram)
A	=	Pool area (square meters)
0.0001	=	Derived constant (see equations D-20 and D-21)

A "Pool Fire Factor" (PFF) was calculated for each regulated flammable liquid and gas (to be applied to gases liquefied by refrigeration) to allow estimation of the distance to the heat radiation level that would lead to second degree burns. For the derivation of this factor, ambient temperature was assumed to be 298 K (25 °C). Other factors are discussed above. The PFF for liquids with boiling points above ambient temperature was derived as follows:

$$PFF = H_c \sqrt{\frac{0.0001}{5,000\pi \ [H_v + C_p(T_b - 298)]}} \qquad \textbf{(D-28)}$$

where: | | | |
|---|---|---|
| 5,000 | = | Radiation per unit area received by the receptor (Watts per square meter) |
| H_c | = | Heat of combustion (Joules per kilogram) |
| H_v | = | Heat of vaporization (Joules per kilogram) |
| C_p | = | Liquid heat capacity (Joules per kilogram-degree K) |
| T_b | = | Boiling temperature (K) |
| 298 | = | Assumed ambient temperature (K) |
| 0.0001 | = | Derived constant (see above) |

For liquids with boiling points below ambient temperature, the PFF is derived as follows:

$$PFF = H_c \sqrt{\frac{0.0001}{5,000\pi \ H_v}} \qquad \textbf{(D-29)}$$

where: | | | |
|---|---|---|
| 5,000 | = | Radiation per unit area received by the receptor (Watts per square meter) |
| H_c | = | Heat of combustion (Joules per kilogram) |
| H_v | = | Heat of vaporization (Joules per kilogram) |
| 0.0001 | = | Derived constant (see above) |

Distances where exposed people could potentially suffer second degree burns can be estimated as the PFF multiplied by the square root of the pool area (in square feet), as discussed in the text.

D.10   BLEVEs

Reference Table 30, the table of distances for BLEVEs, was developed based on equations presented in the AIChE document, *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs*. The Hymes point-source model for a fireball, as cited in the AIChE document, uses the following equation for the radiation received by a receptor:

$$q = \frac{2.2 \ \tau_a \ R \ H_c \ m_f^{0.67}}{4\pi L^2} \qquad \textbf{(D-30)}$$

where: | | | |
|---|---|---|
| q | = | Radiation received by the receptor (Watts per square meter) |
| m_f | = | Mass of fuel in the fireball (kg) |

τ_a	=	Atmospheric transmissivity
H_c	=	Heat of combustion (Joules per kilogram)
R	=	Radiative fraction of heat of combustion
L	=	Distance from fireball center to receptor (meters)
π	=	3.14

Hymes (as cited by AIChE) suggests the following values for R:

R	=	0.3 for vessels bursting below relief valve pressure
R	=	0.4 for vessels bursting at or above relief valve pressure

For development of Reference Table 30, the following conservative assumptions were made:

R	=	0.4
τ_a	=	1

The effects of radiant heat on an exposed person depend on both the intensity of the radiation and the duration of the exposure. For development of the table of distances for BLEVEs, it was assumed that the time of exposure would equal the duration of the fireball. The AIChE document gives the following equations for duration of a fireball:

$$t_c = 0.45 \ m_f^{1/3} \ for \ m_f < 30{,}000 \ kg \tag{D-31}$$

and

$$t_c = 2.6 \ m_f^{1/6} \ for \ m_f > 30{,}000 \ kg \tag{D-32}$$

where:	m_f	=	Mass of fuel (kg)
	t_c	=	Combustion duration (seconds)

According to several sources (e.g., Eisenberg, et al., *Vulnerability Model, A Simulation System for Assessing Damage Resulting from Marine Spills*; Mudan, *Thermal Radiation Hazards from Hydrocarbon Pool Fires* (citing K. Buettner)), the effects of thermal radiation are generally proportional to radiation intensity to the four-thirds power times time of exposure. Thus, a thermal "dose" can be estimated using the following equation:

$$Dose = t \ q^{4/3} \tag{D-33}$$

where:	t	=	Duration of exposure (seconds)
	q	=	Radiation intensity (Watts/m^2)

The thermal "dose" that could cause second-degree burns was estimated assuming 40 seconds as the duration of exposure and 5,000 Watts/m^2 as the radiation intensity. The corresponding dose is 3,420,000 (Watts/m^2)$^{4/3}$-second.

For estimating the distance from a fireball at which a receptor might receive enough thermal radiation to cause second degree burns, the dose estimated above was substituted into the equation for radiation received from a fireball:

$$q = \left[\frac{3,420,000}{t} \right]^{\frac{3}{4}} \qquad \textbf{(D-34)}$$

$$\left[\frac{3,420,000}{t} \right]^{3/4} = \frac{2.2 \; \tau_a \; R \; H_c \; m_f^{0.67}}{4\pi L^2} \qquad \textbf{(D-35)}$$

$$L = \sqrt{ \frac{2.2 \; \tau_a \; R \; H_c \; m_f^{0.67}}{4\pi \left[\dfrac{3,420,000}{t} \right]^{3/4}} } \qquad \textbf{(D-36)}$$

where:

L	=	Distance from fireball center to receptor (meters)
q	=	Radiation received by the receptor (Watts per square meter)
m_f	=	Mass of fuel in the fireball (kg)
τ_a	=	Atmospheric transmissivity (assumed to be 1)
H_c	=	Heat of combustion (Joules per kilogram)
R	=	Radiative fraction of heat of combustion (assumed to be 0.4)
t	=	Duration of the fireball (seconds) (estimated from the equations above); assumed to be duration of exposure

Equation D-36 was used to develop the reference table for BLEVEs presented in the text (Reference Table 30).

D.11 Alternative Scenario Analysis for Vapor Cloud Explosions

According to T.A. Kletz, in "Unconfined Vapor Cloud Explosions" (Eleventh Loss Prevention Symposium, sponsored by AIChE, 1977), unconfined vapor cloud explosions almost always result from the release of flashing liquids. For this reason, the quantity in the cloud for the alternative scenario vapor cloud explosion in this guidance is based on the fraction flashed from the release of a flammable gas liquefied under pressure. The guidance provides a method to estimate the quantity in the cloud from the fraction flashed into vapor plus the quantity that might be carried along as aerosol. The recommendation to use twice the quantity flashed as the mass in the cloud (so long as it does not exceed the total amount of flammable substance available) is based on the method recommended by the UK Health and Safety Executive (HSE), as cited in the AIChE document, *Guidelines for Evaluating the Characteristics of Vapor Cloud Explosions, Flash Fires, and BLEVEs*. The factor of two is intended to allow for spray and aerosol formation.

The equation for the flash fraction, for possible use in for the alternative scenario analysis, is based on the Netherlands TNO document, *Methods for the Calculation of the Physical Effects of the Escape of Dangerous Material* (1980), Chapter 4, "Spray Release." The following equation is provided:

$$X_{vap,a} = \left(X_{vap,b} \ \frac{T_b}{T_l} \right) + \left(\frac{T_b C_l}{h_v} \ \ln\frac{T_l}{T_b} \right)$$ **(D-37)**

where:

$X_{vap,a}$	=	Weight fraction of vapor after expansion
$X_{vap,b}$	=	Weight fraction of vapor before expansion (assumed to be 0 for calculation of the flash fraction)
T_b	=	Boiling temperature of gas compressed to liquid (K)
T_l	=	Temperature of stored gas compressed to liquid (K)
C_l	=	Specific heat of gas compressed to liquid (Joules/kilogram-K)
h_v	=	Heat of evaporation of gas compressed to liquid (Joules/kilogram)

To develop a Flash Fraction Factor (FFF) for use in consequence analysis, compressed gases were assumed to be stored at 25 ºC (298 K) (except in cases where the gas could not be liquefied at that temperature). The equation for FFF is:

$$FFF = \left(\frac{T_b C_l}{h_v} \ \ln\frac{298}{T_b} \right)$$ **(D-38)**

where:

T_b	=	Boiling temperature of gas compressed to liquid (K)
C_l	=	Specific heat of gas compressed to liquid (Joules/kilogram-K)
h_v	=	Heat of evaporation of gas compressed to liquid (Joules/kilogram)
298	=	Temperature of stored gas compressed to liquid (K)

The recommendation to use a yield factor of 0.03 for the alternative scenario analysis for vapor cloud explosions also is based on the UK HSE method cited by AIChE. According to the AIChE document, this recommendation is based on surveys showing than most major vapor cloud explosions have developed between 1 percent and 3 percent of available energy.